

# Investigation of humic acid complexation behavior with uranyl ions using modified synthetic and natural humic acids

By S. Pompe<sup>1,\*</sup>, K. Schmeide<sup>1</sup>, M. Bubner<sup>1</sup>, G. Geipel<sup>1</sup>, K. H. Heise<sup>1</sup>, G. Bernhard<sup>1</sup> and H. Nitsche<sup>1,2</sup>

<sup>1</sup> Forschungszentrum Rossendorf e.V., Institute of Radiochemistry, P.O. Box 510119, D-01314 Dresden, Germany

<sup>2</sup> University of California Berkeley, Lawrence Berkeley National Laboratory, The Glenn T. Seaborg Center, MS 70A-1150, Berkeley, CA 94720, USA

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**Summary.** We investigated the influence of phenolic OH groups on the complexation behavior of humic acid (HA) with  $\text{UO}_2^{2+}$  ions at pH 4. Starting from synthetic HA type M1, natural HA Aldrich, and natural HA Kranichsee, we synthesized modified HAs with blocked phenolic OH groups by derivatization with diazomethane. The partial blocking of phenolic OH groups was confirmed by a radiometric method which quantitatively determined the functional groups and by FTIR spectroscopy. The complexation behavior of the chemically modified and unmodified HAs with  $\text{UO}_2^{2+}$  ions was investigated by time-resolved laser-induced fluorescence spectroscopy. The experimental data were evaluated with the metal ion charge neutralization model. We determined comparable complexation constants for all HAs. Two modified HAs (type M1 and Aldrich) had significantly lower loading capacities for  $\text{UO}_2^{2+}$  ions ( $10.5 \pm 0.9\%$  and  $9.7 \pm 1.6\%$ , respectively) than the corresponding unmodified HAs ( $18.0 \pm 2.0\%$  and  $17.5 \pm 1.6\%$ , respectively). This indicates that the blocking of the phenolic OH groups changes the complexation behavior of HAs.

## 1. Introduction

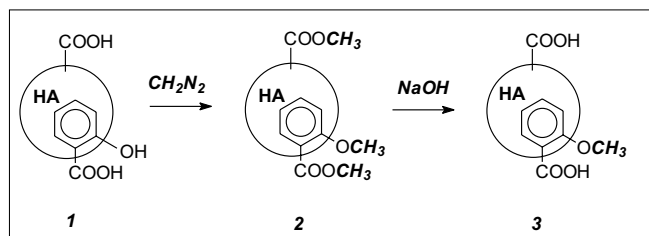
Humic acids (HAs) play an important role in natural interaction processes of metal ions. They are very soluble in the pH range of natural water and possess a high complexing ability toward metal ions. This influences the speciation of metal ions, e.g., actinide ions, and therefore the migration and/or immobilization of these pollutants in the environment. Consequently, the study of the interaction processes between HAs and metal ions is important for a reliable long-term risk assessment for potential nuclear waste repositories and for the remediation of contaminated areas and of facilities from the former uranium mining and milling in Saxony and Thuringia, Germany. Due to the complex nature of HAs the description of their complex formation with metal ions is difficult and not completely understood

up to now. There are various models [e.g., 1–4] describing the metal complexation behavior of HAs. However, these models differ from one another, for instance, in the definition of the complexation reaction and the HA ligand concentration.

We strive to further improve the understanding of the HA-metal ion-interaction. Therefore, we developed HA model substances (HA type M1 [5] and HA type M42 [6]) and investigated their interaction with  $\text{UO}_2^{2+}$  by extended X-ray absorption fine structure [5] and laser-induced fluorescence spectroscopy [6]. We verified that our synthetic HAs are suitable model compounds for natural HAs because they simulate their functionality very well.

In the present work we studied the influence of phenolic OH groups on the complexation behavior of HAs. It is often assumed that only carboxyl groups act as complexing groups in the complexation of HAs with metal ions at pH values below 9 [7]. However, other functional groups, such as phenolic, enolic and alcoholic OH groups as well as amino groups, may also be involved in the complexation process, for instance, via the formation of chelate rings together with carboxylate groups [8]. For our studies we synthesized chemically modified HAs with blocked phenolic OH groups starting from synthetic HA type M1 that was synthesized from glycine, phenylalanine and xylose [5], natural HA from Aldrich (Aldrich, Steinheim, Germany) which was purified according to the purification method described in [9], and natural HA Kranichsee which was isolated from surface water of the mountain bog “Kleiner Kranichsee” (Johanngeorgenstadt, Western Saxony, Germany) [10]. The modification process comprised two steps (a) permethylation of the carboxyl and phenolic OH groups of the original HA with diazomethane resulting in methyl ester and methyl ether groups and (b) hydrolysis of the ester groups in alkaline solution (Fig. 1). We used time-resolved laser-induced fluorescence spectroscopy (TRLFS) to study the complexation behavior of the modified HAs with  $\text{UO}_2^{2+}$  at pH 4 and compared the results to the  $\text{UO}_2^{2+}$  complexation of the original, unmodified HAs. The complexation of HA with uranium(VI) has already been studied by several authors with different methods and complexation models [e.g., 6, 11–16]. However, detailed studies to the influence of different HA

\* Author for correspondence (E-mail: S.Pompe@fz-rossendorf.de).



**Fig. 1.** Reaction scheme for the synthesis of humic acid with blocked phenolic OH groups. (1) – unmodified humic acid, (2) – permethylated humic acid, (3) – humic acid with blocked phenolic hydroxyl groups (HA – humic acid).

functional groups on the complexation behavior of HA with  $\text{UO}_2^{2+}$  using chemically modified HA are not described up to now.

## 2. Experimental

Milli-Q water was used for all experiments (Milli-RO/Milli-Q-System, Millipore, Molsheim, France).

### 2.1 Synthesis of modified humic acids

For permethylation a suspension of the original HA in methanol was reacted under stirring for three hours at  $-5$  to  $5^\circ\text{C}$  with diazomethane, prepared from Diazald® (Sigma-Aldrich, Steinheim, Germany). The solvent was distilled off after three hours. The permethylation procedure was repeated several times and stopped when the incorporation of diazomethane into the HA was completed. The solvent, that was distilled from the reaction mixture, showed then the yellow color of the non-reacted excess of diazomethane. All permethylated HAs were lyophilized and characterized for their functional group content. The permethylated HAs were reacted with 2 M NaOH (Merck, Darmstadt, Germany) at room temperature under inert gas for 8 hours to hydrolyze the ester groups. Then the alkali-insoluble residue was separated by centrifugation. The modified HAs were precipitated with 2 M HCl (Merck), centrifuged, washed, dialyzed using dialysis tubes (Thomapor®, exclusion limit MWCO < 1000, Reichelt Chemietechnik, Heidelberg, Germany), and lyophilized.

It should be noted that in addition to phenolic OH groups also other acidic OH groups, i.e., OH groups substituted

to five-membered heterocycles or enolic OH groups can be methylated with this method. This results also in the formation of nonhydrolyzable methyl ether groups.

### 2.2 Determination of functional groups

The carboxyl group content of the HAs was determined with the calcium acetate method [17]. The proton exchange capacity (PEC) was determined by acid-base titration of HAs which were initially dissolved in alkaline solution. The samples for both methods were prepared and titrated under inert gas. We used an automatic titration system (TPC 2000, Schott, Hofheim, Germany; software TR 600, version 5.02). The phenolic OH groups of the HAs were determined radio-metrically as described in [18].

### 2.3 FTIR measurements

FTIR measurements of the unmodified and modified HAs were carried out with the spectrometer SPECTRUM 2000 (Perkin Elmer Ltd., Beaconsfield, Buckinghamshire, U.K.). Spectra were recorded between 4000 and  $400\text{ cm}^{-1}$ . The samples were pressed as KBr pellets with a diameter of 13 mm.

### 2.4 TRLFS measurements

To study the interaction of the modified and unmodified HAs with  $\text{UO}_2^{2+}$  we determined the fluorescence emission of the uncomplexed  $\text{UO}_2^{2+}$  as a function of the total  $\text{UO}_2^{2+}$  concentration at constant HA concentration. The relative fluorescence signal as a function of the  $\text{UO}_2^{2+}$  concentration was calibrated on solutions that were identical to the solutions of the complexation experiments but did not contain any HA. All experiments were performed in air at  $20 \pm 1^\circ\text{C}$ . The composition of the uranyl humate solutions is summarized in Table 1. The solutions were prepared from stock solutions of HA (0.125 g/L and 0.25 g/L) and of  $\text{UO}_2(\text{ClO}_4)_2$  ( $4.8 \times 10^{-4}\text{ M}$ , in  $4.8 \times 10^{-3}\text{ M HClO}_4$ ). The ionic strength was adjusted to 0.1 M with 1 M  $\text{NaClO}_4$  (p.a., Merck). The pH values were adjusted to pH 4 with NaOH (Merck) and  $\text{HClO}_4$  (Merck). The  $\text{UO}_2^{2+}$  concentrations were determined by ICP-MS analyses.

The uranium species distribution was calculated with the EQ3/6 program [19] based on complex formation constants compiled by Grenthe *et al.* (NEA data base) [20]. It shows

**Table 1.** Composition of the uranyl(VI) humate solutions for the laser spectroscopic investigations of the complexation of  $\text{UO}_2^{2+}$  with the unmodified and modified humic acids type M1 (M1), Aldrich (A2/97) and Kranichsee (KHA).

Humic acid	Modification	$\text{UO}_2^{2+}$ [ $\mu\text{mol/L}$ ]	HA [mg/L]	pH	$\text{I}_{\text{NaClO}_4}$ [mol/L]
M1	original	1.0 – 9.2	10	$3.99 \pm 0.03$	0.1
M1-PB	blocked phenolic OH groups	1.0 – 7.4	10	$3.98 \pm 0.03$	0.1
A2/97	original	1.2 – 12.2	5	$4.00 \pm 0.02$	0.1
A2/97-PB	blocked phenolic OH groups	0.9 – 10.0	5	$3.99 \pm 0.02$	0.1
KHA	original	1.3 – 13.0	5	$3.99 \pm 0.02$	0.1
KHA-PB	blocked phenolic OH groups	1.1 – 13.0	5	$3.99 \pm 0.01$	0.1

that  $\text{UO}_2^{2+}$  is the dominant uranium species at pH 4. Only 2.7% of the total uranium occurs in form of  $\text{UO}_2\text{OH}^+$ . The  $\text{UO}_2\text{OH}^+$  concentration in our experiments is lower than the experimental errors. Therefore, it was not considered for calculating the complexation data. However, because of the high fluorescence yield of  $\text{UO}_2\text{OH}^+$  in comparison to  $\text{UO}_2^{2+}$ , the spectrum of  $\text{UO}_2\text{OH}^+$  was included in the analysis of the fluorescence spectra as described in [6].

A Nd:YAG laser, pulsed with a repetition rate of 10 Hz (GCR 230, Spectra Physics, Mountain View, CA, USA) was used as spectroscopic light source. The fourth harmonic oscillation of the Nd:YAG laser (266 nm) with laser energies  $< 850 \mu\text{J}$  was applied to excite the  $\text{UO}_2^{2+}$  fluorescence. The emission signal was focused into the spectrograph (Model 1235 Acton Research, Acton, MA, USA) by a fiber optic cable. We used a time controlled photodiode array detector (Model 1455 EG&G Instruments, Princeton Applied Research, Princeton, NJ, USA), cooled to  $-30^\circ\text{C}$ . Using a delay generator (Model 9650, EG&G Instruments) the time gate of fluorescence detection was set to open at 200 ns after the excitation pulse for an interval of 1000 ns. The fluorescence signal was measured from 408 to 634 nm. Ten spectra of each sample were collected over 100 laser shots per spectrum and standardized relative to the pulse energy. An average spectrum was calculated from the 10 emission spectra. No emission signals of HA and uranyl humate complexes were observed during the time window of the measurements. We did not observe any quenching effects of the  $\text{UO}_2^{2+}$  ion by self quenching or quenching by the HA in the studied concentration range.

### 3. Results and discussion

#### 3.1 Functional groups

Table 2 summarizes the functional group contents of all HAs. The results show that the phenolic OH groups were only partially blocked during the modification. The modified HAs with blocked phenolic OH groups have 59 to 68% less phenolic OH groups than the original HAs.

After permethylation, functional groups that are capable for methylation but not hydrolyzable were still determined by the radiometric method. These are no carboxyl groups. However, it has not yet been confirmed whether these functional groups are unmodified original phenolic and/or other acidic OH groups of HA or acidic OH groups that are produced during the modification. Furthermore, the number of functional groups which are available for methylation but not hydrolyzable increases during the alkali treatment of the permethylated HAs. This may be due to an unfolding of HA molecules thus uncovering sterically hindered functional groups. A comparison of the carboxyl groups of the corresponding modified and unmodified HAs shows that the modified HAs have a lower carboxyl group content than the original HAs. Possible reasons are a partial decomposition of HA molecules in acid-soluble components, leaching of smaller HA molecules with a higher carboxyl group content from the HA mixture, and/or decarboxylation reactions during the derivatization process. Nevertheless, the molar ratio of phenolic OH to carboxyl groups becomes smaller due to the modification (Table 2). Furthermore, the PEC of the HAs decreases due to the modification of phenolic OH groups and the decrease in the carboxyl group contents.

#### 3.2 FTIR spectroscopy

IR absorption bands indicating the formation of methyl esters and phenyl methyl ethers due to the treatment of the HAs with diazomethane were identified for all permethylated HAs (Fig. 1 (2)). For the HAs with blocked phenolic OH groups (Fig. 1 (3)) we also determined IR absorption bands which are indicative for the phenyl methyl ether formation. However, a clear identification of these absorption bands is difficult because of the overlapping of IR bands of different HA functional groups which results in a few broad bands.

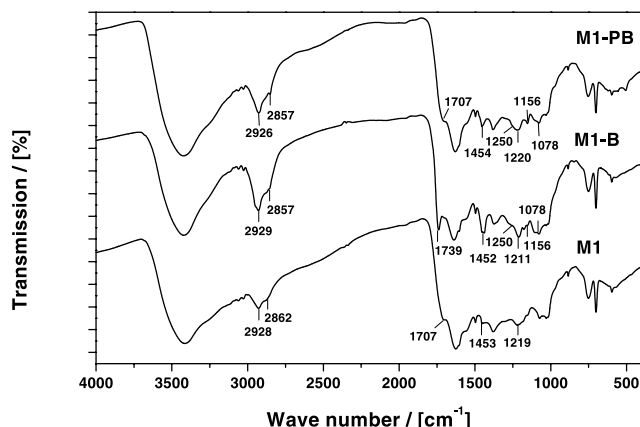
For example, Fig. 2 depicts for HA type M1 the spectra of the original HA (M1), the permethylated HA (M1-B) and the HA with blocked phenolic OH groups (M1-PB). The permethylation of the HA with diazomethane causes an intensity increase of the absorption bands caused by C–H

**Table 2.** Functional group content of the modified and unmodified humic acids type M1 (M1), Aldrich (A2/97) and Kranichsee (KHA).

Humic acid	Modification	Phenolic OH [meq/g]	COOH [meq/g]	PEC [meq/g]	Phenolic OH / COOH
M1	original	$2.4 \pm 0.1$	$1.34 \pm 0.05$	$1.69 \pm 0.10$	1.79
M1-B	permethylated	0.3	$< 0.1^a$	n.m. <sup>b</sup>	–
M1-PB	blocked phenolic OH groups	$0.9 \pm 0.3$	$1.16 \pm 0.03$	$1.35 \pm 0.21$	0.78
A2/97	original	$3.4 \pm 0.5$	$4.41 \pm 0.11$	$5.06 \pm 0.17$	0.77
A2/97-B	permethylated	$0.6 \pm 0.3$	$< 0.1^a$	n.m.	–
A2/97-PB	blocked phenolic OH groups	$1.1 \pm 0.4$	$3.25 \pm 0.05$	$3.58 \pm 0.23$	0.34
KHA	original	$3.9 \pm 0.5$	$4.20 \pm 0.17$	$4.83 \pm 0.18$	0.93
KHA-B	permethylated	0.3	$< 0.1^a$	n.m.	–
KHA-PB	blocked phenolic OH groups	$1.6 \pm 0.4$	$2.83 \pm 0.05$	$3.07 \pm 0.06$	0.57

a: Radiometrically determined [18].

b: n.m.: not measured.



**Fig. 2.** FTIR spectra of the original humic acid type M1 (M1), the permethylated humic acid type M1 (M1-B) and the modified humic acid type M1 with blocked phenolic OH groups (M1-PB). The spectra were shifted along the y-axis for clarity.

stretch (2929 and 2857  $\text{cm}^{-1}$ ) and C–H deformation vibrations (1452  $\text{cm}^{-1}$ ) of  $\text{CH}_3$  groups. This intensity increase is due to the introduction of  $\text{CH}_3$  groups into the HA molecules by methyl ether and ester formation (Fig. 2: M1 and M1-B). After permethylation the absorption band at 1707  $\text{cm}^{-1}$  (C=O stretch vibrations of carboxyl groups) is shifted to 1739  $\text{cm}^{-1}$  due to the formation of ester groups that absorb at higher wave numbers than carboxyl groups. In addition, the absorption band at about 1211  $\text{cm}^{-1}$  (C–O stretching) is sharpened. The enhancement of the absorption bands and shoulders at 1250, 1156 and 1078  $\text{cm}^{-1}$  in the spectrum of M1-B compared to the spectrum of M1 indicates the formation of ether groups including phenyl methyl ethers (1250  $\text{cm}^{-1}$ ). During the hydrolysis of ester groups methanol is released. This can be seen as a decrease of the absorption intensities at 2926, 2857 and 1454  $\text{cm}^{-1}$  in the spectrum of M1-PB compared to the spectrum of M1-B. Due to the hydrolysis of ester groups the absorption band at 1739  $\text{cm}^{-1}$  (C=O stretching of ester groups) which was observed for M1-B is shifted back to 1707  $\text{cm}^{-1}$  (C=O stretching of carboxyl groups) in the spectrum of M1-PB. The absorption bands and shoulders at 1250, 1156 and 1078  $\text{cm}^{-1}$  are enhanced in the spectrum of M1-PB compared to the spectrum of M1 which indicates that the blocking of phenolic OH groups by ether formation was maintained during the hydrolysis reaction.

### 3.3 TRLFS measurements

The experimental data were evaluated with the metal ion charge neutralization model by Kim and Czerwinski [2]. According to this model, the  $\text{UO}_2^{2+}$  ion occupies two proton exchanging sites of the HA molecule [Eq. (1)].



HA(II) represents the HA ligand and  $\text{UO}_2\text{HA(II)}$  stands for the uranyl humate complex. The stability constant  $\beta$  is given by

$$\beta = \frac{[\text{UO}_2\text{HA(II)}]}{[\text{UO}_2^{2+}]_{\text{free}}[\text{HA(II)}]_{\text{free}}} \quad (2)$$

where  $[\text{UO}_2\text{HA(II)}]$  is the uranyl humate complex concentration,  $[\text{UO}_2^{2+}]_{\text{free}}$  the free  $\text{UO}_2^{2+}$  concentration and  $[\text{HA(II)}]_{\text{free}}$  the free HA ligand concentration [2]. This model introduces the loading capacity (LC; Eq. (3)) which represents the mole fraction of maximal available complexing sites of HA under the applied experimental conditions.

$$\text{LC} = \frac{[\text{UO}_2\text{HA(II)}]_{\text{max}}}{[\text{HA(II)}]_{\text{tot}}} \quad (3)$$

$[\text{UO}_2\text{HA(II)}]_{\text{max}}$  represents the maximum concentration of  $\text{UO}_2^{2+}$  which can be complexed with functional sites of HA, and  $[\text{HA(II)}]_{\text{tot}}$  stands for the total molar HA concentration [2]. Thus, the complexation behavior of HA can be described independently of the experimental conditions and the origin of HA. From this it follows, that comparable complexation constants are determined for the complexation of a metal ion with different HAs. This is in contrast to other complexation models, e.g., the polyelectrolyte model [1], where differences in the complexation behavior of HAs are reflected in different stability constants. Using the charge neutralization model, differences in the complexation behavior of HAs under the same experimental conditions are reflected in different LC values. If phenolic OH groups influence the complexation behavior of HA, a significantly lower LC with  $\text{UO}_2^{2+}$  should result for a modified HA with blocked phenolic OH groups than for the corresponding unmodified HA under the same experimental conditions.

The LC values which were graphically determined by linear regression of the experimental data as described in [2] and the mean values of the complexation constants that were computed for each experimental point are given in Table 3. Within their standard deviations, the complexation constants for HA Kranichsee (KHA) and HA Aldrich (A2/97) agree with data published by Schmeide *et al.* [16] for KHA and data for another batch of Aldrich HA [21]. The corresponding  $\log \beta$  values of the modified and unmodified HAs A2/97 and KHA agree well with each other. The values for the modified and unmodified HA type M1 are comparable within their standard deviations. The high standard deviations for all complexation constants are due to experimental errors. Especially experimental errors of the determination of  $[\text{UO}_2^{2+}]_{\text{free}}$  are accumulated in  $\log \beta$  (Eq. (2)), because  $[\text{UO}_2^{2+}]_{\text{free}}$  is included in the determination of

**Table 3.** Loading capacities (LC) and complexation constants ( $\log \beta$ ) for the complexation of  $\text{UO}_2^{2+}$  with the unmodified and modified humic acids type M1 (M1), Aldrich (A2/97) and Kranichsee (KHA) determined by TRLFS (pH 4, I: 0.1 M  $\text{NaClO}_4$ , T:  $20 \pm 1$  °C).

Humic acid	Modification	LC / [%] <sup>a</sup>	$\log \beta^a$
M1	original	$18.0 \pm 2.0$	$6.14 \pm 0.30$
M1-PB	blocked phenolic OH groups	$10.5 \pm 0.9$	$6.56 \pm 0.38$
A2/97	original	$17.5 \pm 1.6$	$6.20 \pm 0.56$
A2/97-PB	blocked phenolic OH groups	$9.7 \pm 1.6$	$6.22 \pm 0.60$
KHA	original	$15.6 \pm 1.9$	$6.16 \pm 0.76$
KHA-PB	blocked phenolic OH groups	$12.4 \pm 1.9$	$6.10 \pm 0.58$

a: Deviations =  $2\sigma$ .

[ $\text{UO}_2\text{HA(II)}$ ] and LC, and therefore also in the determination of  $[\text{HA(II)}]_{\text{free}}$ , as described in [2]. The experimental errors have its origin, for instance, in laser energy measurements, photon counting and in the determination of the total  $\text{UO}_2^{2+}$  concentration.

Comparing the LC values of the modified and unmodified HAs it is obvious that M1-PB ( $10.5 \pm 0.9\%$ ) and A2/97-PB ( $9.7 \pm 1.6\%$ ) have a significant lower LC than the corresponding original HAs ( $18.0 \pm 2.0\%$  and  $17.5 \pm 1.6\%$ , respectively). KHA-PB has also a lower LC ( $12.4 \pm 1.9\%$ ) than the original HA ( $15.6 \pm 1.9\%$ ), but, this difference is smaller. These results show that the modified HAs have a smaller mole fraction of maximal available complexing sites than the original HAs. Figure 3 shows, exemplary for the modified and unmodified HAs type M1 and Aldrich, the plots of the mole ratios  $[\text{UO}_2\text{HA(II)}]/[\text{HA(II)}]_{\text{tot}}$  against  $[\text{UO}_2^{2+}]_{\text{tot}}/[\text{HA(II)}]_{\text{tot}}$  which illustrate the LC values. With increase of the total  $\text{UO}_2^{2+}$  concentration the mole ratio  $[\text{UO}_2\text{HA(II)}]/[\text{HA(II)}]_{\text{tot}}$  approaches for all HAs a value which represents LC of HA (Table 3).

The results of these investigations confirm earlier results found for the  $\text{UO}_2^{2+}$  complexation of a modified (phenolic OH blocked) and a unmodified HA type M1, that were obtained by another derivatization method [21].

Different LC values of the modified and unmodified HAs indicate that the blocking of phenolic OH groups changes the complexation behavior of HAs. It can be concluded that

phenolic OH groups can be involved in the complexation process of HAs with  $\text{UO}_2^{2+}$  under the applied conditions. The reduction, on a percentage basis, of the molar ratios of phenolic OH to carboxyl groups due to the derivatization is higher than the reduction of the LC values of the modified HAs compared to the unmodified HAs. That points to the fact that not all modified functional groups would contribute to the interaction of the unmodified HAs with  $\text{UO}_2^{2+}$ . The different influence of the modification of phenolic OH groups on the LC which was observed, for instance, for the HAs of Kranichsee and Aldrich (Table 3) may be due to structural dissimilarities of HAs, depending on their origin.

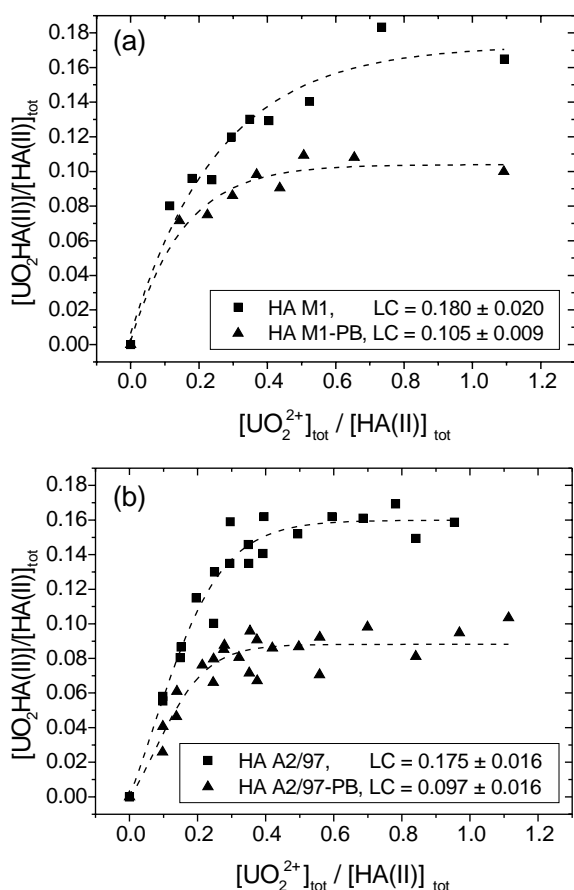
At pH 4, phenolic OH groups are probably protonated due to their high  $\text{pK}_a$  values. In addition to carboxyl groups, intermolecular hydrogen bonds between hydrogen atoms of phenolic OH groups and oxygen atoms of  $\text{UO}_2^{2+}$  ions may contribute to the complex formation of the unmodified HAs with  $\text{UO}_2^{2+}$  in solution. However, it cannot be excluded that phenolic OH groups act also as complexing ligands upon proton release. This tendency may be increased by mesomeric substituent effects which can enhance the acidity of phenolic OH groups. Furthermore, it is possible that in the unmodified HAs neighboring phenolic OH groups and/or phenolic OH groups in ortho-position to carboxyl groups complex the  $\text{UO}_2^{2+}$  ion by formation of either a five-membered or a six-membered chelate ring. Nevertheless, also steric effects, i.e., steric hindrances, may contribute to a change of the complexation behavior of HAs after blocking the phenolic OH groups.

The assumption that phenolic OH groups are involved as complexing ligands in the interaction between HA and  $\text{UO}_2^{2+}$  is supported by several studies [22–24]. The authors describe the complexation of  $\text{UO}_2^{2+}$  with simple phenolic compounds which may occur as structural elements of HA. Bartušek *et al.* [22] observed the complex formation of  $\text{UO}_2^{2+}$  with catechol (1,2-dihydroxybenzene), resorcin (1,3-dihydroxybenzene) and phenol starting at about pH 3. Roßberg *et al.* [24] studied the complexation of  $\text{UO}_2^{2+}$  with pyrogallol (1,2,3-trihydroxybenzene) at pH 4.8 and catechol at pH 5 by EXAFS spectroscopy, and determined structural parameters for 1 : 1 complexes. These investigations show that phenolic OH groups are able to react as complexing ligands in the acidic pH range.

## 4. Conclusions

For the first time, the influence of phenolic OH groups on the  $\text{UO}_2^{2+}$  complexation by HA was investigated using chemically modified synthetic and natural HAs with partially blocked phenolic OH groups. The complexation of the modified HAs with  $\text{UO}_2^{2+}$  was studied in comparison to the  $\text{UO}_2^{2+}$  complexation of the unmodified HAs at pH 4. Significant lower LC values, with  $\text{UO}_2^{2+}$  were determined for the modified HAs type M1 and Aldrich than for the corresponding original, unmodified HAs (Table 3). That indicates a lower amount of maximal available complexing sites of the modified HAs compared to the unmodified HAs.

Hence, it can be concluded that the modification of phenolic OH groups changes the complexation behavior of HA with  $\text{UO}_2^{2+}$ . Already at pH 4, phenolic OH groups contribute



**Fig. 3.** Illustration of the loading capacity (LC) of the modified (M1-PB) and unmodified (M1) synthetic humic acid type M1 (a) and the modified (A2/97-PB) and unmodified (A2/97) humic acid from Aldrich (b).

to the interaction between HA and  $\text{UO}_2^{2+}$  ions. We assume that the blocking of phenolic OH groups will more change the complexation behavior of HA in the alkaline pH region where phenolic OH groups may act as deprotonated complexing ligands. Furthermore, it can be concluded that the selective modification of HA functional groups represents a powerful tool for a more detailed investigation of the interaction processes between HA and metal ions.

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